

Volume compression of cerium up to 4 GPa

Anil K Singh

Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017, India

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Abstract. The volume compression of cerium was remeasured up to 4 GPa. The bulk modulus and its pressure derivative, as calculated from the compression data, are respectively 19 ± 1 GPa and -10 for γ -cerium. The $\gamma \rightarrow \alpha$ transition was found to occur at 0.77 GPa with 0.2 GPa hysteresis for the $\gamma \rightarrow \alpha$ transition. The bulk modulus of the α -phase immediately after the transition is very low (14 GPa) and its pressure derivative large (-10). The pressure derivative of the bulk modulus becomes normal beyond 1.2 GPa.

The anomalous volume compression of γ -cerium has been explained in terms of a continuous delocalization under pressure of $4f$ electrons. The average fraction of $4f$ electrons delocalized under pressure has been estimated. The pressure variation of the gap between the $4f$ electrons and the Fermi level has been estimated from the compression data and found to be 0.04 eV/GPa. An estimate of the valency of α -cerium suggests that it approaches $+4$ state as the pressure is increased. The valency prior to the $\alpha \rightarrow \gamma$ transition is estimated to be 3.8 ± 0.1 .

1 Introduction

A series of compressibility measurements by Bridgman (1927, 1948a, 1948b, 1951) revealed certain interesting properties of cerium at high pressures. First of all, the compressibility of the low-pressure phase (γ -phase) was abnormal in that it increased with the increase of pressure. In the vicinity of 1 GPa, a phase transition accompanied by a large volume change was observed. It was shown later by x-ray diffraction methods (Lawson and Tang 1949) that the transition was isostructural, i.e. the crystal symmetry remained unchanged during the transition. While the general features of the high-pressure behaviour of cerium were unmistakable in most of Bridgman's work, the results of various studies showed significant differences as regards the magnitude of the compressibility, the transition pressure, and the kinetics of transition. These differences were attributed to the varying degrees of sample purity. As samples of higher purity became available, the emphasis shifted from compressibility measurements to other aspects such as phase-diagram studies, melting behaviour, and the triple point (Jayaraman 1965). Compressibility measurements on high-purity samples of cerium remained largely unattempted. The commonly quoted compressibility data, even today, are those presented by Gschneidner (1964), which are based on Bridgman's (1948a, 1948b) results. It must be noted that in these studies the $\gamma \rightarrow \alpha$ transition was observed at 1.22 GPa with a volume change of nearly 8% as compared to the currently accepted values of 0.77 GPa for the transition pressure and 13% for the volume change at the transition. For these reasons it was considered worthwhile to remeasure the compressibility of cerium on high-purity samples.

The interest in the compressibility data has been revived recently by the suggestion that α -cerium undergoes interconfiguration fluctuation (ICF). The compression-shift mechanism (Hirst 1974) plays an important role in preventing the system (γ -cerium) in a pure configuration state $4f^7$ from going into another pure configuration state $4f^8$.

The compressibility data for γ - and α -cerium [up to](#) 4 GPa, were obtained here with the use of a piston-cylinder apparatus. The results are compared with data available in the literature. The anomalous compression of γ -cerium is attributed to a continuous delocalization under pressure of $4f$ electrons. The compression of the

a-phase, especially in the pressure region immediately after the transition, is also anomalous in that the pressure derivative of the bulk modulus is very large. It is suggested that such behaviour can arise if metastable γ -phase coexists with α -phase over a small pressure range after the $\gamma \rightarrow \alpha$ transition. The compressibility data have been used to estimate the number of delocalized 4f electrons as a function of pressure in both γ - and α -phases. Some of the implications of the present results for Hirst's (1974) theory are discussed.

2 Experimental details

The apparatus used in this work was similar to that described elsewhere (Vaidya and Kennedy 1970). In brief, the pressure vessel consisted of a tungsten carbide cylinder (Carboloy 883, 1.27 cm inside diameter, 5.08 cm outside diameter, and 5.08 cm long). A cylindrical sample, 1.0 cm in diameter and 1.25 cm long, weighing 6.7800 g was wrapped in an 0.12 cm thick indium sheet. The two ends of the sample were covered with 0.1 cm thick indium discs. The extrusion of indium past the piston was prevented by the use of pyrophyllite mitre rings at both ends. The piston displacement was measured with a pair of dial gauges with a precision of 0.00005 cm. The details of the sample assembly, a discussion of the pressure distribution in the cell, and other relevant experimental details are presented elsewhere (Singh and Kennedy 1974a, 1974b). It may be recalled that the design of the cell assembly used in the present experiment has given good results earlier; for example, it was possible to resolve two transitions, 0.3 GPa apart, in calcite and determine the compressibility in this small pressure range.

The cerium metal used in this study was 99.8% pure (from Research Organic/Inorganic Chemical Corp., USA). The major impurities are listed in table 1. The cylindrical samples, 1.0 cm in diameter and 1.25 cm long, were machined. The sample surface was protected by mineral oil at the time of machining. Care was taken to avoid heating of the sample during machining. The machined samples were cleaned and annealed in vacuum at 400 °C for 4 h and then quenched in air.

To determine the compressibility of the γ -phase the piston displacement, d , was measured as a function of pressure, p , by increasing the pressure in steps of 0.07 GPa. After a nominal pressure of 0.75 GPa was reached, the pressure was decreased in steps of 0.07 GPa and the piston displacement noted with the decreasing pressure. The d - p curve was corrected for friction by taking the midpoints of the hysteresis loop. From these data the loss of pressure through friction was estimated and found to increase linearly with pressure. The standard error in d , as estimated from the d - p data from four independent runs was 1 μ m. It must be noted that any possible influence of the $\gamma \rightarrow \alpha$ transition on the d - p data in an outstroke run was avoided, by keeping the highest pressure for the instroke run less than the pressure of transition.

The d - p data have to be corrected for piston displacement arising from instrumental factors, such as compression of the pistons, elastic dilatation of the bore of the pressure vessel, and compression of the pressure-transmitting medium and the pyrophyllite mitre rings. This can be best done by making measurements with reference to a standard material the compressibility of which is known with a high degree of accuracy. For this purpose, in a separate experiment, the cerium sample was replaced

Table 1. Major impurities present in the cerium sample.

Element	Si	Cr	Mn	Fe	Ni	Zr	Mo
Content/ppm	50	40	20	350	30	150	800
Element	Ba	La	Pr	Nd	Tb	Hf	Pb
Content/ppm	200	25	50	15	50	25	30

by an equal volume of ammonium chloride, whilst the volumes of indium and pyrophyllite were kept unchanged. The $d-p$ curve for ammonium chloride was then determined. From the $d-p$ data for the sample and the standard, the compressibility of the sample was calculated as discussed in the next section.

A separate series of experiments was conducted to determine the pressures of the γ - α transitions. The $d-p$ data were obtained at intervals of 0.07 GPa up to pressures well beyond the region of the γ - α transition. A typical $d-p$ curve is shown in figure 1. The γ - α transition pressure was read from the instroke $d-p$ curve, and corrected for friction by using the frictional loss versus instroke pressure curve obtained in the experiments aimed at the measurement of the compressibility of the γ -phase. It might appear more reasonable to use the outstroke data in figure 1 to estimate the friction correction. This was not done because the pressure of the α - γ transition is significantly lower than the pressure of the γ - α transition. As a result, if the instroke and outstroke $d-p$ data (figure 1) are used, the friction correction will be overestimated. This would lead to an underestimation of the pressure of the γ - α transition.

The $d-p$ data were obtained up to a nominal pressure of 5.0 GPa for the determination of the compressibility of the α -phase. The $d-p$ data were corrected for the piston displacement arising from the instrumental factors by using $d-p$ data for ammonium chloride.

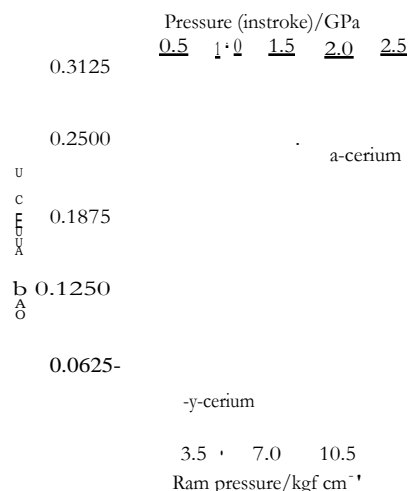


Figure 1. Piston displacement plotted against, ram pressure for γ - and α -cerium.

3 Data processing

It can be easily shown (Singh and Kennedy 1975) that the compressibility of the sample material is given by

$$X_s(p) = \frac{V_s(p)}{V_s(0)} - \frac{V_s(p)}{V_s(0)} \frac{S(p)}{S(0)} \frac{m(p)}{m(0)} \quad (1)$$

The suffixes s and i denote, respectively, the sample and the standard, X is the compressibility, $v(p) = V(p)/V(0)$, i.e. the ratio of the volume at pressure p to the, volume at 1 atm. $S(p)$ is the effective area of the piston face at pressure p, $m(p)$ is the slope of the $d-p$ curve. The volumes of the sample and the standard are so adjusted that $V(0) = V_s(0) = V(0)$. In the derivation of equation (1) it is assumed that the volumes of the pressure transmitter (indium) and the pyrophyllite mitre rings are the same for the runs with the sample and with the standard.

The slopes $m(p)$ were calculated from the $d-p$ data corrected for friction by making use of the relation

$$m(p) = \frac{d(P_1) - d(P_2)}{P_1 - P_2} \quad (2)$$

where $p = 4(p_1 + p_2)$.

The values of $x_{s(p)}$ were calculated with the use of equation (1). To start with, Bridgman's values, as given by Gschneidner (1964), were used. The $V_s(p)$ values were calculated by using a modified Murnaghan equation (Vaidya et al 1971) with $B_0 = 17.3$ GPa, $B_0' = 6.48$, and $B_0'' = 0.568$ GPa⁻¹ for ammonium chloride. A polynomial of the form

$$X_S(P) = [X_0 + X_1(P) + X_2P^2 + \dots] \quad (3)$$

was fitted to the x_s versus p data.

The following relation for $v_s(p)$ can be obtained by integrating equation (3) and letting $u_s = 1$ at $p = 0$:

$$v_s(p) = \exp[-(X_0p + \frac{1}{2}X_1P^2 + \frac{1}{3}X_2P^3 + \dots)] \quad (4)$$

The $x_s(p)$ values were recalculated from equation (1) with the use of the values of $v_s(p)$ obtained from equation (4). Two iterations gave a set of $x_{s(p)}$ and $v_s(p)$ values which did not change on further iteration.

The expression for $v_s(p)$, similar to that given by equation (4), for the α -phase can be derived by integrating equation (3) and using the condition $v_s(p) = v_t$ at $p = p_t$, where v_t is the fractional volume change at the $\gamma \rightarrow \alpha$ transition, and p_t is the pressure of the $\gamma \rightarrow \alpha$ transition. This gives the following results:

$$v_s(p) = \exp[-(X_0p + \frac{1}{2}X_1P^2 + \frac{1}{3}X_2P^3 + \dots) + C]$$

where

$$C = -\ln v_t - [X_0p_t + \frac{1}{2}X_1P_t^2 + \frac{1}{3}X_2P_t^3 + \dots] \quad (5)$$

4 Results

4.1 Compression of γ -cerium

The compressibility of γ -cerium in the pressure range 0-0.7 GPa was calculated as described in section 3 and the results are given in table 2. The standard error in $[m_s(p) - m_s(p)]$ was 0.003 cm GPa⁻¹. The error in $B_s(p)$ varies from 6% at 0.1 GPa to 4% at 0.7 GPa, while the error in $(1 - u_s)$ varied from 1.2% to 5% over the same pressure range. These errors were estimated from the scatter of the experimental data. Any uncertainty in the knowledge of $v_t(p)$ will lead to a systematic error in $u_s(p)$ and $B_s(p)$. The uncertainties in $B_s(0)$ and $B_s'(0)$ are, respectively, 3% and 15%.

Table 2. $X(p)$ and $v(p)$ as a function of p for γ -cerium.

P GPa	$m_s(P)$ 10^{-3} cm GPa ⁻¹	$m_s(P)$ 10^{-3} cm GPa ⁻¹	$v_s(p)$	$X_s(p)$ GPa ⁻¹	$v_s(p)$	$X_s(P)$ GPa ⁻¹	$B_s(P)$ GPa
0.0						0.0523	19.12
0.1	74.07	75.63	0.9941	0.0575	0.9946	0.0555	18.02
0.2	76.09	73.58	0.9885	0.05537	0.9890	0.0586	17.06
0.3	78.01	71.22	0.9832	0.05339	0.9831	0.0622	16.08
0.4	80.01	68.54	0.9780	0.05155	0.9770	0.0665	15.04
0.5	82.13	65.56	0.9731	0.04983	0.9705	0.0718	13.93
0.6	84.15	62.26	0.9684	0.04822	0.9635	0.0777	12.87
0.7	86.17	58.65	0.9638	0.04671	0.9562	0.0844	11.85

The experimental results presented in table 2 contain all the information necessary to recalculate $v_s(p)$ and $B_s(p)$ with any other set of $v_i(p)$ values.

It is seen from table 2 that the compressibility of γ -cerium increases (and the bulk modulus decreases) as the pressure is increased from 1 atm to 0.7 GPa. The first pressure derivative of the bulk modulus is nearly -10. This behaviour is quite unlike that of a normal material which shows an increase in bulk modulus with the increase of pressure.

The bulk modulus and volume compression of γ -cerium as a function of pressure are shown in figure 2.

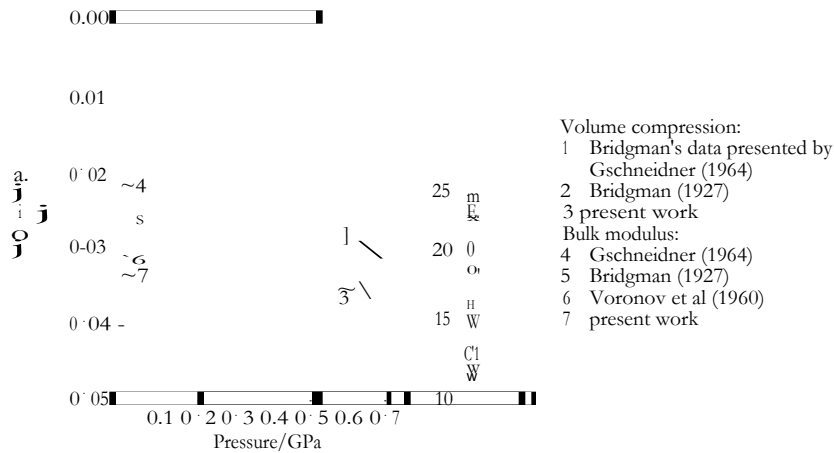


Figure 2. The variation of volume compression and bulk modulus with pressure for γ -cerium.

4.2 Transition pressure

The analysis of the $d-p$ data from four independent runs gives 0.77 ± 0.02 and 0.57 ± 0.02 GPa respectively for the $\gamma - \alpha$ and $\alpha - \gamma$ transitions. This means that $\gamma \rightarrow \alpha$ transitions show an intrinsic hysteresis of 0.20 GPa. The volume change at the $\gamma \rightarrow \alpha$ transition was $13 \pm 0.2\%$.

4.3 Compression of α -cerium

The compressibility, the bulk modulus, and the volume compression in the range 1-4 GPa are listed in table 3. The estimated uncertainty in the compressibility is ± 0.0005 . The v , versus p data are plotted in figure 3; the curve shows a large curvature after the $\gamma \rightarrow \alpha$ transition, indicating a large B_0 . The bulk modulus as a function of pressure is shown in figure 4. It is seen that B_0 in the pressure range 1-2 GPa is -10, and decreases to -4 beyond 2 GPa.

Table 3. Compression data for α -cerium.

p GPa	x GPa ¹	B_0 GPa	$\frac{V(0)-V(p)}{V(0)}$	p GPa	x GPa ¹	B_0 GPa	$\frac{V(0)-V(p)}{V(0)}$
1.05	0.0600	16.7	0.1857	2.60	0.0318	31.4	0.2367
1.24	0.0534	18.7	0.1943	2.78	0.0310	32.3	0.2412
1.44	0.0478	20.9	0.2025	3.00	0.0304	32.9	0.2458
1.63	0.0433	23.1	0.2093	3.18	0.0300	33.3	0.2502
1.82	0.0398	25.1	0.2156	3.38	0.0295	33.9	0.2546
2.02	0.0368	27.2	0.2215	3.57	0.0291	34.4	0.2588
2.21	0.0347	28.8	0.2268	3.77	0.0284	35.2	0.2630
2.34	0.0330	30.3	0.2317				

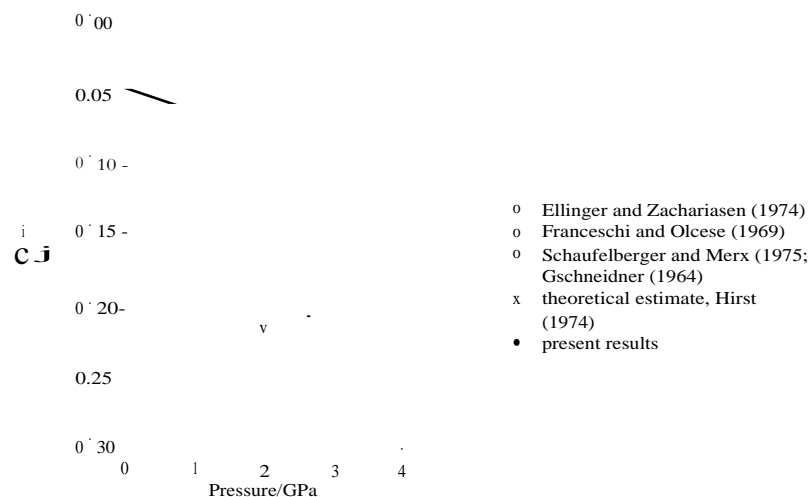


Figure 3. Pressure dependence of the volume compression of α -cerium.

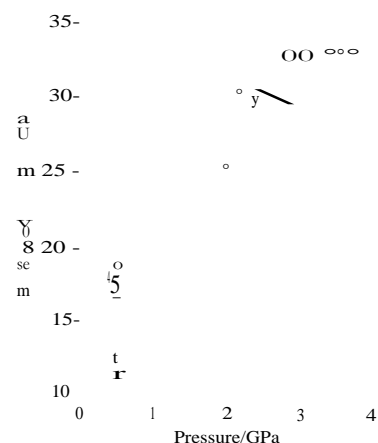


Figure 4. Pressure dependence of the bulk modulus of α -cerium.

5 Comparison with other data

5.1 γ -cerium

The first reports on the compressibility of γ -cerium (Bridgman 1922, 1923) indicated that its behaviour was quite normal in that the compressibility decreased with the increase of pressure. Measurements made later (Bridgman 1927) showed a transition at 0.75 GPa, a pressure remarkably close to the currently accepted value of 0.77 GPa for the γ - α transition pressure. This measurement also revealed the abnormal compression behaviour of the γ -phase. The measurements on samples of supposedly 'higher purity' (Bridgman 1948b) confirmed the abnormal compression of the γ -phase but gave 1.2 GPa for the pressure of the γ - α transition. While summarizing earlier work, Bridgman (1948b) stated that the transition did not run sharply in the earlier work (Bridgman 1927). In his compilation of the compression data Gschneidner (1964) used Bridgman's (1948b) results. For closer comparison, the volume compression and the bulk modulus data are shown in figure 2. It is seen that the volume compression obtained in the present work is significantly higher than those listed by Gschneidner (1964). However, the present values are in better agreement

with those of Bridgman (1927). The present values of the bulk moduli are in reasonably good agreement with those obtained by ultrasonic technique (Voronov et al 1960). The present value of the compressibility at 1 atm is 0.0525 GPa^{-1} which compares very well with the value of 0.050 GPa^{-1} obtained by Beecroft and Swenson (1960) and the value of 0.05 GPa^{-1} obtained by a strain-gauge technique under truly hydrostatic pressure (Leger et al 1975).

The pressures of the $\gamma \rightarrow \alpha$ transitions and the volume change associated with the transition as obtained by various investigators are listed in table 4. In the present experiments the $\gamma \rightarrow \alpha$ and $\alpha \rightarrow \gamma$ transitions were found to occur, respectively, at 0.77 ± 0.02 and 0.57 ± 0.02 GPa. These values are in good agreement with those obtained by Gschneidner et al (1962), Livshits et al (1960), and Bridgman (1951). The $\gamma \rightarrow \alpha$ transition pressure differs from that for $\alpha \rightarrow \gamma$ by 0.2 GPa . Beecroft and Swenson (1960) did not observe appreciable hysteresis in the $\gamma \rightarrow \alpha$ transitions and obtained a value of 0.675 GPa for the $\gamma \rightarrow \alpha$ transition pressure. It is interesting to note that this value agrees well with the average of the pressures of the $\gamma \rightarrow \alpha$ transitions obtained in this experiment. Herman and Swenson (1958), however, observed appreciable hysteresis in the $\gamma \rightarrow \alpha$ transitions. Their values for the volume change associated with the $\gamma \rightarrow \alpha$ transition seem to vary between 12% to 16%. A value as low as 8% has been reported by Bridgman (1948b) and by Likhter et al (1958).

Table 4. Comparison of various transition parameters.

p GPa ^{a)}	$M_{\alpha \rightarrow \gamma}$ GPa	p_{γ} (averaged) GPa	$\frac{V(0) - V(p)}{V(0)}$ i	Method ^s	Reference ^b
0.767 ± 0.008	0.568	-	0.136		Gschneidner (1962)
0.779	0.583	-	0.140	D, J	
-	-	0.675 ± 0.01	0.141 ± 0.002	P-C	Beecroft (1960)
-	-	0.7	0.12-0.16, (< 0.165)	P-C	Herman (1958)
0.9	$0.6 (20^\circ \text{C})$	0.79	0.08	P-C	Likhter (1958)
0.76	$0.59 (20.5^\circ \text{C})$	-	-	R	Livshits (1960)
-	-	0.75	-	P-C	Bridgman (1927)
-	-	1.22	0.08		Bridgman (1948b)
0.78	0.57	-	-	R	Bridgman (1951)
0.77	$0.57 (22^\circ \text{C})$	-	0.130 ± 0.002	P-C	present value
0.757	-	-	0.13		Gschneidner (1964)

^{a)} D, dilatometric; P-C, piston-cylinder; R, resistivity.

^{b)} Only the first author is listed.

5.2 α -cerium

The volume compression and the bulk modulus of the α -phase are plotted as functions of pressure in figures 3 and 4, respectively, together with the data obtained by other investigators. It is seen that Bridgman's data (Gschneidner 1964) show smaller compression than those in the present experiments in the pressure range 0.76 to 3.0 GPa. The x-ray data of Franceschi and Olcese (1969) deviate considerably from the present compression data. The x-ray data of Schaufelberger and Merx (1975) give higher compression than the present data but are closer to the present data than those of Franceschi and Olcese.

One of the features which has been observed in all the present runs is that the v_s - p curve has a large curvature starting immediately after the $\gamma \rightarrow \alpha$ transition and continuing until a pressure of around 2 GPa is reached. B_0 is nearly 10 in this

pressure range. Beyond 2 GPa the curvature in the v_s - p curve diminishes considerably. B_0 is -4 above 2 GPa, The data from ultrasonic experiments (Voronov et al 1960) suggest that B_0 immediately after the transition is -14, which is of the same order as 10 obtained in the present experiment. The factors which are likely to give rise to a large curvature in the v_s - p curve will be discussed in the next section.

6 Discussion

6.1 γ -cerium

A plot of B_0 as a function of the atomic number for the rare-earth elements (figure 5) indicates that B_0 values for cerium, europium, and ytterbium deviate considerably from the trend set by the other elements in the group. As discussed earlier in this paper, B_0 is also anomalous in that it is negative. Thus both B_0 and B_0 are anomalous for cerium. This, however, can be explained satisfactorily if it is assumed that in the γ -phase a continuous pressure-induced 4f delocalization takes place. Since there is a volume contraction associated with the delocalization of 4f electrons (as observed at the $\gamma \rightarrow \alpha$ transition), the measured volume compression is the sum of the volume change arising from the normal compression and the volume change arising from the delocalization of the 4f electrons; it is the latter which makes the compression behaviour abnormal.

The idea that the delocalization of 4f electrons takes place continuously in the γ -phase appears reasonable from band-structure considerations (Gschneidner 1964; MacPherson et al 1971; Coqblin and Blandin 1968). In γ -cerium the sixfold degenerate ($J = 1$) 4f states are split by intra-atomic Coulomb interaction and exchange, such that one of the states lies below the Fermi level. With decreasing volume the centre of gravity of these states moves upwards with respect to the Fermi level. The energy gap, E , between the Fermi level and the 4f level is 0.076 eV (Wilkins et al 1962) at 1 atm. This means that there are nearly 0.05 4f electrons per atom delocalized by thermal excitation at room temperature and 1 atm. Since E decreases with increasing pressure, the number of delocalized 4f electrons also increases.

In order to discuss the compression behaviour of the γ -phase in terms of the pressure-induced delocalization of 4f electrons let us assume, for the sake of simplicity, that the pressure-volume relation is adequately defined by a second-degree polynomial:

$$v - 1 = -ap + bp^2, \quad (6)$$

such that $a = B_0$ and $B_0 = (2b/a^2) - 1$. Let the normal compression, i.e. the compression in the absence of a 4f delocalization be given by

$$v_{\gamma} - 1 = -a_{\gamma}p + b_{\gamma}p^2, \quad (7)$$

0.08

Cal 0.06

a 0.04.

$\frac{b}{a}$ 0.02

La Pr Pm Eu Tb Ho Tm Lu
Ce Nd Sm Gd Dy Er Yb

Figure 5. Plot of compressibility against the atomic number for the rare-earth elements.

The volume change arising from the 4f delocalization can be represented by a similar equation:

$$v_f - 1 = -a_f p + b_f p^2. \quad (8)$$

The measured volume compression is the sum of $(v_n - 1)$ and $(v_f - 1)$. Thus,

$$v_{\text{exp}} - 1 = u_n + a_f - 2 - (a_n + a_f)p + (b_n + b_f)p^2. \quad (9)$$

The experimentally obtained bulk modulus and its pressure derivatives are given by

$$B_{0, \text{exp}} = \frac{1}{a_n + a_f} \quad (10)$$

and

$$B_{0, \text{exp}} = 2(a_n + a_f)^{-1}. \quad (11)$$

Thus $B_{0, \text{exp}}$ will be less than the normal bulk modulus, $1/a_n$, if the 4f delocalization involves a decrease in the volume. Further, $B_{0, \text{exp}}$ can be positive or negative depending on the sign and the magnitude of b_f . Since $B_{0, \text{exp}}$ is negative it is concluded that b_f is negative and $|b_f| > |b_n|$.

The normal volume compression, $(u_n - 1)$, can be estimated with a reasonable accuracy by taking the average of the volume compressions of lanthanum and praseodymium, the nearest neighbours of cerium in the Periodic Table. If the compression data for lanthanum and praseodymium (Gshneidner 1964) are used, one obtains $a_n = 0.03695 \text{ GPa}^{-1}$ and $b_n = 0.002493 \text{ GPa}^{-2}$. On using 19.13 GPa and -10.37 as the present values, respectively, of $B_{0, \text{exp}}$ and $B_{0, \text{exp}}$ and the above values of a_n and b_n , equations (10) and (11) give $a_f = 0.01533 \text{ GPa}^{-1}$ and $b_f = -0.01530 \text{ GPa}^{-2}$.

The value of $(v_f - 1)$ in the γ -phase can now be calculated as a function of pressure from equation (8) with the above values of a_f and b_f .

The number of the delocalized 4f electrons, $Z(p)$, can be estimated from the $(u_f - 1)$ data if it is assumed that $(v_f - 1)$ depends linearly on $Z(p)$. Let a volume change, X , be associated with a complete delocalization of a 4f electron (one electron per atom). The number of such electrons for a volume change $(u_f - 1)$ is then given by

$$Z(p) = \frac{u_f - 1}{X} + Z(0), \quad (12)$$

where $Z(0)$ is the number of 4f electrons delocalized at 1 atm by thermal excitation at room temperature. As estimated earlier in this section, $Z(0) = 0.05$.

The value of A can be estimated by making use of some additional information. The volume change associated with the $\gamma - \alpha$ transition is 13% and the valency of α -cerium immediately after the transition is 3.67 (Gschneidner 1977). If the valency, $(3+Z_t)$, of cerium just before the $\gamma - \alpha$ transition is known, then A can be calculated from the relation

$$A = 0.13 / (67 - Z_t) \quad (13)$$

Z_t is the value of $Z(p)$ just before the $\gamma \rightarrow \alpha$ transition.

The values of Z_t and A were obtained by an iterative process. To start with, $Z_t = 0.12$ was assumed. This gave $A = 0.2364$. The value of Z_t was then calculated from equation (12) with $A = 0.2364$. A few cycles of iteration gave $A = 0.2476$.

which did not change on further iteration. The value of X can also be estimated from the ionic radii of Ce^+ and Ce^0 , which are, respectively, 1.034 \AA and 0.941 \AA (Landelli 1961). The value of X calculated from these data is 0.2463 which agrees very well with the value obtained here. It might appear more appropriate to estimate X from metallic radii rather than ionic radii. However, the metallic radius for fully collapsed α -cerium is not available. Further, since we are interested in the fractional volume change, the error introduced by taking ionic radii instead of metallic radii is, to a first approximation, cancelled.

The values of $Z(p)$ calculated with $X = 0.2476$ as a function of pressure are shown in figure 6. As the pressure is increased, $Z(p)$ increases from 0.053 at 1 atm to 0.14 at 0.77 GPa . Such estimates of $Z(p)$ were first made by Gschneidner and Smoluchowski (1963) who obtained 0.11 for $Z(p)$ at 0.77 GPa .

The variation with pressure of E , the energy gap between the Fermi level and the $4f$ narrow band, can also be estimated from these data. For this purpose, let us assume that the delocalization of $4f$ electrons is caused by thermal excitation and also that the number of delocalized $4f$ electrons is small such that E_F is not much affected. If the system is approximated by a simple two-level system separated by an energy gap E , then the numbers of electrons in the higher and lower energy levels, n_1 and n_2 respectively, are related through the Boltzmann number:

$$n_1 = \exp[-E/kT] \quad (14)$$

with $n_1 = Z(p)$ and $n_2 = 1 - Z(p)$, the following expression results for $Z(p)$:

$$Z(p) = \frac{1}{1 + \exp[E(p)/kT]} \quad (15)$$

Since the present discussion is limited to a small range of pressure, viz 1 atm to 0.77 GPa , the pressure dependence of E can be assumed to be linear:

$$E(p) = E(0) + E'(0)p. \quad (16)$$

The $Z(p)$ data were fitted to equation (15) with $E(0) = 0.076 \text{ eV}$. A value of $-0.04 \text{ eV GPa}^{-1}$ was obtained for $E'(0)$. This means that $E(p)$ just before the $\gamma \rightarrow \alpha$ transition is 0.05 eV .

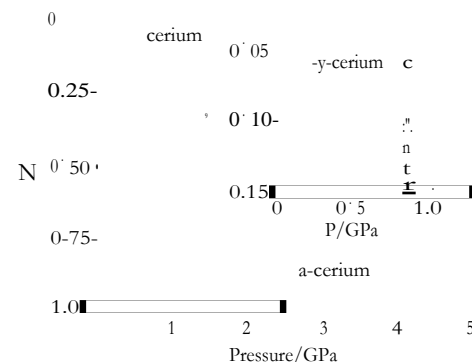


Figure 6. The number of delocalized $4f$ electrons, $Z(p)$, as a function of pressure for γ - and α -cerium.

6.2 α -cerium

The pressure-volume data (figure 3) in the range 0.77 to 2 GPa are anomalous in that B_0 is very large (nearly 10 , figure 4). The question arises whether such a behaviour is characteristic of α -cerium which is in ICF state (Hirst 1974), or arises

because of some other factors such as an incomplete $\gamma \rightarrow \alpha$ transition. It is important, at this stage, to include the information available from high-pressure x-ray diffraction studies. Ellinger and Zachariasen (1974) observed the metastable β -cerium coexisting with α -cerium in the pressure range 0.8 to 1.4 GPa. The large curvature of the v_{β} - p plot immediately following the $\gamma \rightarrow \alpha$ transition can arise from the presence of metastable γ -cerium. The metastable β -phase can transform to α -cerium on further increase of pressure, giving rise to a volume decrease corresponding to the transition. It should be noted that the plot of electric resistance versus pressure (Bridgman 1951) also exhibits a large curvature immediately after the transition. This behaviour can also be explained qualitatively by the presence of some metastable γ -cerium after the $\gamma \rightarrow \alpha$ transition.

The data above 2 GPa are characteristic of the α -phase since the metastable γ -phase does not exist above 2 GPa (Schaufelberger and Merx 1975). The present value of B_0 above 2 GPa is 4 which agrees reasonably well with 5.4, the value obtained by Schaufelberger and Merx (1975) from high-pressure x-ray diffraction data.

The value of $Z(p)$ for the α -phase can be estimated by a procedure similar to that followed for the γ -phase. The estimation of the normal volume compression, v_{α} , for the α -phase is complicated because of a volume decrease of 13% at the transition. The values of $v_{\alpha}(p)$ for the α -phase were estimated as follows. The values of a_{α} and b_{α} obtained earlier in this paper were used to calculate B_{α} and B'_{α} . This gave $B_{\alpha} = 27.06$ GPa and $B'_{\alpha} = 2.65$. With these values of B_{α} and B'_{α} inserted in the Murnaghan equation, the pressure p_0 at which $v_{\alpha} = 0.18$ was calculated. The value of 0.18 for v_{α} was equal to the volume decrease at 0.77 GPa in the γ -phase plus the decrease in volume at the transition. A value of 7.10 GPa was obtained for p_0 . The value of $v_{\alpha}(p)$ at a pressure p was calculated by inserting $(p + p_0 - 0.77)$ GPa for pressure in the Murnaghan equation with $B_{\alpha} = 27.06$ and $B'_{\alpha} = 2.65$.

The physical significance behind the procedure for estimating $v_{\alpha}(p)$ is explained graphically in figure 7. The solid line represents the experimental v - p curve. At the point X_1 , $v = 0.18$ and $p = 0.77$. The broken line represents the v_{α} - p curve obtained from the average of the volume compressions of lanthanum and praseodymium. The pressure corresponding to X_2 is p_0 . Thus, the point X_1 on the experimental v - p curve corresponds to the point X_2 on the v_{α} - p curve. A point X at pressure p on the experimental v - p curve therefore corresponds to a point X' with $(p_0 + p - 0.77)$ as the p coordinate on the v_{α} - p curve.

The number, $AZ(p)$, of the 4f electrons delocalized by the change of pressure from 0.77 to p as calculated by putting $X = 0.2476$. The values of $Z(p)$ were calculated by adding 0.67 to $OZ(p)$, and are shown in figure 6.

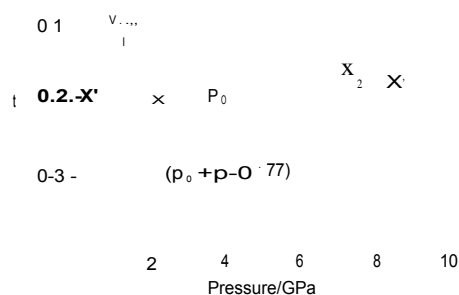


Figure 7. Method of calculating $v_{\alpha}(p)$ for the α -phase.

The reliability in the estimation of $v_{\infty}(p)$ for the α -phase depends on the validity of the procedure adopted for predicting the value of $v_{\infty}(p)$ after the phase transition outlined in figure 7. To test the validity of this method, the bulk moduli of the high-pressure phases were estimated for a large number of systems for which the bulk moduli of both the low- and the high-pressure phases had been measured experimentally. A comparison of the predicted values of the bulk moduli of the high-pressure phases with the corresponding experimental values indicates that the predicted values are consistently higher than the experimental values. Hence, the present estimates of $v_{\infty}(p)$ are likely to be on the high side. This would mean that the values of $Z(p)$ in figure 6 have been overestimated. The estimate of $v_{\infty}(p)$ for the α -phase will also contain errors arising from the errors in B_0 and B'_0 for the low-pressure phase, because an extrapolation over a pressure range of 7 GPa is required. The overall uncertainty in the estimate of $Z(p)$ is -5%.

6.3 Compression data and the ICF state

In a recent paper Hirst (1974) parameterized electronic energy as a function of volume and also added a term containing volume-dependent elastic energy. For cerium, these terms together (compression-shift mechanism) suggest a discontinuous pressure-volume relation near the configuration crossover. If a volume-dependent bulk modulus, which increases with decreasing volume, is considered, then an ICF state following the configuration crossover is predicted. The increase in the bulk modulus with decrease in volume prevents γ -cerium, assumed to be in a pure configuration state $4f^7$, from going to another pure configuration state $4f^8$.

Hirst (1974) calculated the v - p curve taking into account the compression-shift mechanism. For comparison with the present data the values of $(1 - v)$ obtained from figure 5 of Hirst are also shown in figure 3. It is seen that the theoretically calculated v - p curve also exhibits a large curvature immediately after the γ - α transition. The bulk modulus is low and its pressure derivative large in this region. The value of $(1 - v)$ at the transition is, however, low when compared to the experimental value because of two factors. Firstly, a value of $24 \cdot 5$ GPa for the bulk modulus of the γ -phase has been assumed in the calculations, whereas the experimental value is close to 20 GPa. Secondly, the Birch equation with $B_0 = 4$ has been used, whereas the experimental value of B'_0 is -10. The similarity between the experimental v - p relation for α -cerium and that predicted from the theory is very close, and this might be taken to suggest that the large curvature of the v - p curve following the γ - α transition is a characteristic feature of the ICF state. However, as has been pointed out in section 6.2, this feature can also be explained qualitatively on the basis of the metastable γ -phase coexisting with the α -phase. An accurate determination of the v - p curve for the γ -phase alone by x-ray diffraction technique can resolve this ambiguity. Such an experiment is at present being carried out.

The theoretical estimates of $Z(p)$ indicate that $Z(p)$ increases with increasing pressure and approaches $Z = 1$ near 6 GPa. The estimates of $Z(p)$ made from the present compression data are in good agreement with those predicted theoretically from the model based on the compression-shift mechanism.

The γ -phase of cerium has been considered in Hirst's theory as a pure configuration state $4f^7$ with $dZ/dv = 0$. It is seen from the present analysis that a volume-dependent Z has to be assumed if the abnormal volume compression of the γ -phase is to be explained. The average value of dZ/dv for the γ -phase is nearly one-fourth its value in the α -phase.

7 Conclusion

The compression data obtained in this investigation are in good agreement with some of the earlier data. The anomalous behaviour of the compression data in the γ -phase is confirmed.

The anomalous behaviour of the γ -phase is explained by assuming that a continuous delocalisation under pressure of 4f electrons takes place. The analysis of the compression data on the basis of this model suggests that the energy gap between the 4f level and the Fermi level decreases at a rate 0.04 eV GPa^{-1} , and the number of delocalized 4f electrons just before the γ - α transition is 0.14 electrons/atom.

The compression curve immediately after the transformation is abnormal in that the pressure derivative of the bulk modulus is large; above -2.0 GPa the compression curve is normal. The theoretical estimates of the compression curve (Hirst 1974) show a trend very similar to that observed experimentally. This might be taken to indicate that the experimentally observed behaviour of the compression curve immediately after the transition is characteristic of the ICF state. However, such a behaviour can also be explained if metastable γ -phase coexists with the α -phase, and transforms to the α -phase on further increase of pressure.

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